HEAT STERILIZABLE
IMPACT RESISTANT CELL
DEVELOPMENT

JET PROPULSION LABORATORY
CONTRACT NO. 951296

REPORT FOR FOURTH QUARTER, 1969

and

FIRST QUARTER 1970

OCTOBER 1, 1969 to MARCH 31, 1970

ESB, INCORPORATED
EXIDE MISSILE AND ELECTRONICS DIVISION
RALEIGH, NORTH CAROLINA

April 1970

ESB, Incorporated
The Carl. F. Norberg Research Center
Yardley, Pennsylvania

The Exide Missile and Electronics Division
Raleigh, North Carolina

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Prepared By: G. F. Nordblom
Section Leader

A. M. Chreitzberg
Asst. Dir. of Engrg.

Approved By: G.S. Hartman
Dir. of Engrg.

April 1970

NOTICE

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ABSTRACT, CONCLUSIONS, AND RECOMMENDATIONS

Five and twenty-five ampere-hour prototype cells capable of 4,000 g shock have been wet heat sterilized 72 hours at 135°C successfully and shipped to JPL for impact tests in the range 2,000 through 4,000 g.

Charge acceptance was 10-20% lower than expected on the small size cells, but performance of the 25 AH cells on formation charge and discharge was at expected voltages and capacities.

Sixteen ampere-hour cells cycled at 100% depth of discharge after wet heat sterilization maintain capacity best to 69 cycles when ZnO/Ag weight ratio is in range 1.2 to 1.5 to 1. Electrolyte limitation restricts performance of higher ratio cells if sufficient electrolyte is not provided for the excess of ZnO. Appendix 1 is a statistical analysis of capacities delivered to date in the 27 cell experiment.

70 ampere-hour rechargeable primary cells have passed sine, and random vibration tests at JPL. In vertical vibration plane at 25 g voltage drops occurred unless both positive and negative plate tabs were insulated with plastic sleeves. 27 cells

have been manufactured for long term reliability tests.

Twenty-five ampere-hour cells, designed for intermediate cycle life after heat sterilization and 8-month interplanetary cruise have demonstrated 168 cycles at 50% depth of discharge with only a short stand life after sterilization. Similar cells, cycled before heat sterilization give about 50% less cycle life. A third group, having a wet stand life with six deep cycles of 9 months, is being environmentally tested at JPL before cycling per mission profile.

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FABRICATION AND TESTING OF CELLS

I. DEVELOPMENT OF HIGH IMPACT 5.0 AH CELLS--TASK 9

A. Objective and Past Work

5.0 AH cells must be developed to meet JPL Specification GMP-50437-DSN-C, including simulated hard landing impacts of 2,800 ± 200 g from 115 ± 3 feet/second and JPL Engineering Memorandum 342-70. Non-high impact cells have delivered 11.0 AH at 3.3 amperes to 1.25 volts at 43 WH/lb of sealed cell after 72 hours heat sterilization at 135°C. Impacts of 2,400 g were survived with Ag sheet plate structures in the cell. Prototypes have zirconium sheet positive plate structures and chemically etched Ag negative plate structures. Output in the same cell volume is reduced to 7 AH by mechanical structure. Massive negative grids are preamalgamated but zirconium positive structure is untreated.

B. Prototype Fabrication

Twelve Model 361 prototype cells were assembled in the final design, and ten cells have been shipped to JPL for impact tests in the range 2,000 to 4,000 "g". All cells survived wet sealed heat sterilization for 72 hours at 135°C in air with no electrolyte leakage. During formation charge without clamps for support the maximum cell case bulge was 18-mils indicating relatively low cell pressures at this crucial stage. Table I presents the electrical cycling data obtained prior to shipment. Charge acceptance was 10-20% lower than expected on an average. One cell (S/N 7) leaked between recharge and discharge and electrolyte loss from that cell has decreased capacity further. This cell was rejected for impact testing.

Development testing during fabrication and parts acceptance included burst pressure tests after heat sterilization 72 hours at 135°C on dummy cells having no plates but case and cover seal per drawing 361-2000. Eight assemblies tested gave low (median) high burst pressures of 125 (149) 178 psig. Case failure occured in the broad jar walls with cracks developing along the vertical jar corners.

Etched Ag grids for the negative plates varied widely in weight, ranging from a nominal 9.7 grams to plus 1.8 and minus 0.9 grams. Consequently, each grid was weighed and wet pasted with 100% inspection to drawing active material weight and thickness tolerances. Mean negative plate thickness (43 mils) was 7 mils greater than drawing requirement and could not be decreased further with the active material mix selected. The pack tightness was increased as a result from a design wet thickness allowance per layer of SWRI-GX membrane of 3.0 mils to 2.6 mils actual. Free void for electrolyte in the cell still was sufficient for activation of the cells with 1.0 cc electrolyte per gram Ag active material in the positive plates.

C. Future Work

- Test 10 cells at 2,000, 3,000, and 4,000 g shock levels at JPL using the decrease in loaded voltage as a measure of plate damage.
- Cycle 2 cells at ESB as no shock controls.
- Redirect effort to delete production of thirty (30) cells for delivery to JPL.

II. DEVELOPMENT OF HIGH CYCLE LIFE 48 AH CELLS--TASK 10

A. Objectives and Past Work

Wet heat sterilizable 48 AH cells must be developed to meet the requirements of JPL Specification 50436-DSN-B. Operating requirements in sequence are one year prelaunch storage, heat sterilization 72 hours at 135°C, flight acceptance test, launch, 9-month interplanetary cruise, soft landing, and 400 cycles 50% depth of discharge after a 12-hour charge. An experiment with 27 16 AH cells representing one third replication of a 3^4 factorial design has been initiated and carried through 16 cycles. Effects on capacity maintenance due to teflonation in sintered negatives at levels 5, 7, and 9 percent teflon, wet membrane allowance at levels 2.0, 2.4, and 2.8 mils per layer, and electrolyte concentration at levels 41, 43, and 45% were not statistically significant. Capacity decreases from cycle 1 to cycle 5 were larger with decreasing ZnO/Ag weight ratio at levels 0.9, 1.2, and 1.5.

B. Factorial Experiment: Cycles 29-69.

During the reporting period 100% depth cycling of the factorial cells progressed through cycle 69. Figures 1-4 give decay of discharge capacity at the C/3 rate to 1.25 volts after constant current charges at the C/20 rate to 2.05 volts. At cycle 46 the cells were let down, weighed accurately to determine electrolyte loss during cycling if any, then adjusted to a net increase of 5% more than the original wieght of electrolyte at initial activation. Table II gives as a function of cell design the cycle 1 and cycle 47 weights of electrolyte in each cell. The initial cycle 1 cell electrolyte weights were calculated and controlled on the basis that all free void in separator, plates, and other space between plates would be filled with electrolyte. Using the initial weight values of Table II the equation for electrolyte weight for the 27 factorial cells was determined by computer analysis to be--

$$WT = 85.98 + .2111\ TF + 5.0778\ TH + 7.0500\ R + 1.3778K$$

where--

TF = (% teflon - 7)/2
TH = (GX wet thickness in mils - 2.4)/.4
R = (ZnO/Ag weight ratio - 1.2)/.3
K = (% KOH - 43)/2

and all levels were weighted at -1, 0, and +1. The coefficients of the equation show the relative order in which design restraints control electrolyte weight and perhaps capacity when electrolyte limited--

$R > TH > K > TF$ in the ratio 7.05:5.08:1.38:0.21

Electrolyte limitation was indeed eliminated in high ratio cells by the 5% addition of electrolyte and the capacity of cells with R = 1.5 then became equal or greater than cells with R = 1.2 The ratio effect was significant as a quadratic response before and as a linear response after addition of 5% more electrolyte by weight.

The Appendix gives a report of the statistical analysis performed by North Carolina State University. The analysis and the experimental results support the use of 1.5:1.0 ZnO/Ag weight ratio in cells cycled at 100% depth to better maintain capacity but suggests the extra ZnO weight per cell will be useless unless sufficient electrolyte is provided to prevent electrolyte limitation. A negative wrap and no absorber in either positive or negative plate, common to all the factorial cells, did not prevent electrolyte limitation. An absorber wrapped around the positive and unaffected by wet heat sterilization would prevent electrolyte limitation if the free void is sufficient to make up the deficiency of electrolyte in the GX separator system.

The percent teflon in the sintered negative plates has not yet been found significant when tested at levels 5, 7, and 9% by weight to 69 cycles.

Membrane wet thickness allowance, inversely proportional to pack tightness, is also not significant when tested at levels 2.0, 2.4, and 2.8 to 69 cycles.

KOH concentration (41, 43, and 45% near saturation with ZnO) is not significant to date.

C. Future Work

Cycling will continue to failure of cells by short so that the effect of the variables on life to short can be analyzed. Four cells have shorted to date in range 58 to 65 cycles at one year wet life including 72 hours heat sterilization at 135°C, and two each are from the 0.9 and 1.2 ZnO/Ag ratio groups.

Redirection of the contract is being negotiated to eliminate scale-up to 48 AH and permit more testing of 20 AH cells. Prime test variables and design factors will be inclusion of positive plate absorbers, positive wrap, extended negative plate edges, higher ZnO/Ag ratios, wedge or contoured negative plates, cycle routine, and improved distribution of electrolyte with wicks.

III. DEVELOPMENT OF RECHARGEABLE PRIMARY 70 AH CELLS--TASK 11

A. Objectives and Past Work

Sealed wet heat sterilizable 70 AH cells have been developed to the prototype stage to meet the requirements of JPL Engineering Memorandum 342-71. A six cell battery having cells potted into an aluminum chassis is now on test at JPL and to date has been subjected without failure to sweeping sine vibration of 5 g 17 to 50 cps, 15 g 50 to 100 cps, and 35 g 100 to 2000 cps, and random vibration, 200 g shock, and 100 g acceleration tests are scheduled at JPL.

B. Environmental Tests at JPL

During sine and random vibration erratic open circuit voltages and loaded voltages were observed on the cells of the 6-cell battery. The single test variable in the 6-cell battery was the type of sleeving insulating plate tabs. In the tabulation below the cell sleeving type is contrasted to the observed voltages, and the conclusion is drawn that the best cell design requires 10 mil sleeving on both positive and negative plate tabs.

Sleeving Design	Cell S/N	Open Circuit Volts	Loaded Voltage-Volts 10A	20A	40A
No sleeving	13,14,15	Low	1.52-	1.37-	1.14-
Sleeve on positives	16	Normal	1.54	1.47	1.25
Sleeve on negatives	17	Low	1.64	1.45	1.23
Sleeve on positives and negatives	18	Normal	1.63	1.47	1.34

C. Manufacture of Reliability Cells

A release to manufacture 27 Model 364[1] cells (70 AH) for reliability tests was given to the ESB Pilot Plant based on electrochemical tests[2] and the early environmental test data. These cells have been manufactured to ESB D/L 364 Revision F which includes changes of positive and negative plate weight to agree with actual observed on the prototype cell plates, and the addition of 10-mil FEP sleeving on both (+) and (-) plate tabs. After final seal minute cracks were observed in the covers of 4 of 27 cells. Corrective action was directed on MRR 10981 and will require a mold change to increase the inside cover groove radius from .030 maximum to .060. Cracking occurs when the cross-section of the flange is marginally low and mold stresses are not eliminated in the molding cycle. All other manufacturing operations were to print and to process specification requirements.

D. Future Work

Reliability cell tests now schedule three 9-cell groups stored up to 5 months charged, discharged, or on float. At intervals of 1, 3, and 5 months all cells will be given a capacity measuring cycle and then returned to storage. Each storage 9-cell group will be divided into three 3-cell groups: one small group each stored at 50, 70, and 90°F. Capacity loss curves will be generated at 3 temperatures for the 3 storage conditions and will be a measure of the wet life of this 9 layer GX separator system. At the end of the contract the cells will be shipped to JPL for further testing.

IV. DEVELOPMENT OF HEAT STERILIZABLE HIGH IMPACT 25 AH CELLS--TASK 12

A. Objectives and Past Work

This task requires the development and test of 25 AH sealed Ag-ZnO cells capable of 72 hour wet heat sterilization, 9-months interplanetary cruise, planet entry, a hard landing shock of 4,000 "g" in any axis plus 90 50% DOD cycles per JPL Engineering Memorandum 342-68. Cell packs tested without sterilization in Lucite jars at 4,200 "g" failed only in the terminals forward shock vector with bending of plate struts. Gassing of negative plates containing massive Ag etched grids was solved by preamalgamation of the grids before assembly.

B. Assembly and Formation Cycling of Prototype Cells

Molding acceptance test parts were received from the vendor and passed dimensional tests. Eight jars, covers, subcovers, and vent plugs were sealed per ESB drawing 362-2000, the prototype cell final assembly, with 160 cc's cell electrolyte. The dummy cells were then heat sterilized 72 hours at 135°C supported only on the broad faces and not at all on the cover flanges. No visible leakage occurred but a weight loss of 1.1 to 1.6 g water was observed and attributed to diffusion through the case.

Following the weight test the dummy cells were fitted with pressure lines and burst individually with air pressure. The mean burst pressure was 84 psig with a minimum of 68 and a maximum of 94 psig. The failure mode was as expected near the vertical corners of the broad side walls.

Positive and negative plate fabrication was identical in process to the procedures for the SAH cell of Task 9. The negative active material was baked at an oven temperature of 270°F and then damp pasted into the openings of the etched grids. No sintering of the grid was essential to maintain maximum strength in the pure Ag negative grid. Each grid had been amalgamated 1% by weight from a mercuric iodide-potassium iodide bath. The completed negative plates (with and without amalgamation) were assembled into 3-plate cells and given a formation charge and discharge. Figure 5 shows the charge and discharge performance and the gassing characteristics. The cell with unamalgamated negatives began gassing at 25% capacity input and gassed throughout charge. The amalgamated negatives gassed only at the end of charge. Discharge capacities at 0.1 amp/in^2 were almost identical, 2.58 to 2.59 AH or 0.50 AH/g ZnO, 76% theoretical, considered nominal for the formation cycle.

Assembly of the 12 prototype cells was per print and process specifications without dimensional conflicts or sealing problems. All survived 72 hours heat sterilization at 135°C without visible leakage. On the subsequent formation charge all cells began to bulge immediately after start of charge and were vented when the bulging reached 100-mils, after 2-hours charge time. The cells remained vented overnight and were then resealed with pressure gages. During the remainder of the formation cycle, only one of 12 cells developed sufficient pressure (46 psig) to require venting.

A summation of the formation cycle data is given in Table III. Average charge acceptance was 0.41 AH/g Ag. Discharge capacities at the 12 amp rate were 0.30 to 0.40 AH/g Ag, acceptable but more variable than desired. Second cycle input was just about the same as the previous discharge capacity.

Eight of the 12 cells were shipped to JPL for shock tests in the range 2,000 to 4,000 "g". The four cells at ESB will be cycled as non-shocked controls.

C. Future Work

Cells which survive the environmental tests at JPL will be returned to ESB for automatic 50% depth of discharge cycling. The goal is 90 cycles on a test routine of 10 hours charge and 2 hours discharge, 2 cycles per day for 45 days.

Redirection of the task has deleted all deliverable cells. At the completion of the cycling tests and delivery of design documentation, estimated to be August 14, 1970, this task will be complete.

V. DEVELOPMENT OF 25 AH MEDIUM CYCLE LIFE CELL--TASK 13

A. Objective and Past Work

JPL Engineering Memorandum 342-68 (less the 4,000 g shock) requires a 25 AH cell capable of wet heat sterilization sealed 72 hours at 135°C, 9-month interplanetary cruise, planet entry, soft landing, followed by 90 cycles of 50% depth of discharge. The ESB Model 379 cell, developed and tested in five designs, has delivered up to 168 cycles after heat sterilization at 50% depth on a routine of 2 cycles per day, 10 hour charge, 2 hour discharge. Design variables giving best performance are 1L Pellon 2530W absorber and 7L Southwest Research Institute GX wrapped on positives, $49 g/in^3$ negative active material density, no platelock and no pre-test.

B. Engineering and Production Documentation

All action items resulting from the final design review on September 30, 1969 have been completed. Drawings and specifications were up-dated and released in final form. A full set was submitted to JPL on 17 October 1969 as ESB D/L 379 Revision E.

C. Failure Analyses of 25 AH Test Cells

Twenty-five cells, 5 each in 5 designs, were tested as three test groups:

- Test Group I — No Plate-Lock, No Pre-Test (15 cells)
- Test Group II — With Pre-Test Before Heat Sterilization (5 cells)
- Test Group III — With Plate-Lock (5 cells)

Cycling tests on groups I and II have been completed to failure of at least one cell of each design type. Table IV is a life history of Test Group II. Cells were dissected to establish failure modes and then the separator system membrane was analyzed for silver content. Table V summarizes the life history, design features, and analytical values of silver (and mercury) found in each membrane layer of the cells dissected to date. Test group I with no plate-lock or pre-test accumulated less silver deposit than test group II cells even though the ratio of cycles completed was almost 2:1 more for group I. All pretest cycling was 100% in depth and at higher rates of discharge. Total Ag deposited in all layers of the separator system varies from .026 to .036 $mg/in^2/AH$ discharge capacity in the group I cells. Table IV gives the life history of the pretest cell group at time of analysis. In effect the group II cells were cycled more intensively than the group I cells and silver penetration (following the increased rate of current flow) increased to .045 to .072 $mg/in^2/AH$ in all layers. In general, in both groups cells having 9 layers GX failed by loss in ability to deliver 50% rated capacity to the test end voltage while cells with 7 layers GX failed by a combination of silver, zinc, and mercury penetration.

D. Tests on 25 AH Cells with Plate-Lock

One cell each of the five design types had an epoxy plate-lock installed to cement the bottom of the plates to the jar. This added structure is designed to prevent plate damage during vibration in the vertical plane but could also be a contaminant in the system capable of interaction during heat sterilization or charged stand.

The five cells, S/N 21 through 25, were activated 4-10-68, heat sterilized 72 hours at 135°C, cycled at 100% depth at ESB until 5-31-69 and then shipped to JPL for environmental tests per JPL Engineering Memorandum 342-68. On 1-16-70 the wet life was 9 months 6 days and the charged stand since last charge was 7 months 15 days. Table VI summarizes the life history at ESB and at JPL up to the point of environmental shock and vibration tests.

This data confirms little deterioration which can be ascribed to the epoxy plate-lock. The mean charged stand and cycling loss in 9 months of wet life is 3.4% per month which is recoverable on charge and comparable to[3] cells with no plate-lock. Based on the cycle 5 discharge at 8 A to 1.25 v ($\sim C/3$ rate) discharge efficiencies decrease with following design changes:

Wrap	Absorber	Design Layers GX	Negative Density	Positive Plate Efficiency AH/g Ag
+	1L	7L	42	.34
+	1L	7L	49	.29
+	0	9L	42	.28
-	0	9L	42	.26
-	0	9L	49	.25

The top two designs also gave maximum cycle life in test groups I and II.

E. Future Work

During the next quarter shock, vibration, and acceleration tests will be performed at JPL on test group III cells; then cells will be returned to ESB for 50% depth of discharge cycling on a 10 hour charge/2 hour discharge test to establish cycle life after a complete mission profile. Estimated task completion date is August 31, 1970.

TABLE I

FORMATION CHARGE AND DISCHARGE 5.0 AH HIGH IMPACT CELLS
BEFORE SHOCK TESTS

Test	Unit	Low Cell	Median n = 12	High Cell
1. Open Circuit Voltages	volts			
As Manufactured		-0.193	-0.100	+0.107
Before Heat Sterilization		+0.731	+0.750	+0.760
After Heat Sterilization (1)		-0.002	+0.005	+0.016
2. Formation Charge	AH			
• First Stage Input 0.15A to 2.00V		4.34	6.25	6.60
• Partial Discharge 0.4A to 1.70V		0.85	.120	1.20
• Recharge Input 0.15A to 2.00V		2.00	2.50	3.26
• Net Input, (all steps)	AH	6.55	7.27	7.68
	AH/gAg	.31	.35	.37
3. Discharge Capacity	AH			
• 3.2A to 1.25V	AH	5.12 (2)	5.60	5.76
• 0.65A to 1.25V	AH	.34	.52	.70
• Total Both Rates	AH	5.46	6.12	6.46
	AH/g	.26	.29	.31

Notes: (1) After 72 hours at 135°C
(2) Developed leak case to cover between recharge and discharge.

TABLE II
ORIGINAL ELECTROLYTE WEIGHT AND WEIGHT AFTER
5% ADDITION OF ELECTROLYTE AFTER 47th 100% DOD CYCLE

% Teflon	% KOH	GX Allow Mils	ZnO/Ag Ratio						Cell S/N
			0.9		1.2		1.5		
9	41	2.0			78.7	82.6			24
		2.4	77.4	81.3					9
		2.8					99.1	104.1	12
	43	2.0	74.6	78.3					27
		2.4					94.2	98.9	3
		2.8			90.7	95.2			15
	45	2.0					88.7	93.1	21
		2.4			88.7	93.1			6
		2.8	84.8	89.0					18
7	41	2.0					85.8	90.1	17
		2.4			83.0	87.2			20
		2.8	83.7	87.9					5
	43	2.0			81.1	85.2			11
		2.4	77.0	80.9					23
		2.8					98.2	103.1	8
	45	2.0	74.4	78.1					14
		2.4					95.8	100.6	26
		2.8			92.4	97.0			2
5	41	2.0	74.8	78.5					1
		2.4					90.7	95.2	13
		2.8			88.1	92.5			25
	43	2.0					88.6	93.0	4
		2.4			84.5	88.7			16
		2.8	85.1	89.4					19
	45	2.0			82.3	86.4			7
		2.4	80.7	84.7					10
		2.8					98.3	103.2	22

TABLE III

FORMATION CHARGE AND DISCHARGE 25 AH HIGH IMPACT CELLS
BEFORE SHOCK TESTS

Test	Unit	Low Cell	Median n = 12	High Cell
1. Open Circuit Voltages	volts			
As Manufactured		-0.351	-0.009	+0.143
Before Heat Sterilization		+ .758	+ .765	+ .773
After Heat Sterilization (1)		+ .008	+ .010	+ .016
2. Formation Charge				
• First Stage Input 0.5A to 2.00V	AH	24.2	26.3	30.0
• Partial Discharge 2.0A to 1.70V	AH	4.0	6.0	6.0
• Recharge Input 0.5A to 2.00V	AH	14.9	18.7	22.2
• Net Input (all steps)	AH	37.4	39.8	42.4
	AH/gAg	.385	.410	.436
3. Pressure on Formation Charge (2)	psig (max)	5	32	46 (3)
4. Discharge Capacity				
• 12A to 1.25V	AH	28.4	31.8	35.6
• 2.4A to 1.25V	AH	1.6	2.6	3.3
• Both Steps (total)	AH	30.0	34.8	38.9
	AH/gAg	.308	.358	.400
5. Cycle 2 Recharge				
• 0.5A to 2.00V	AH	30.9	35.1	37.2

Notes: (1) All cells heat sterilized wet sealed 72 hours at 135°C
(2) Cells gassed on formation charge, vented 16 hours, then resealed.
(3) Cell S/N 9 vented second time before discharge.

TABLE IV

LIFE HISTORY OF PRETEST GROUP CELLS

Test Date 1969	Test Completed	Unit	Test Data by Cell S/N				
			2	8	11	15	18
3-17	Formation charge	AH	30.2	27.7	34.1	34.5	42.7
3-25	Partial discharge	AH	4.9	- 8.4	- 3.6	- 3.6	- 5.3
3-26	Recharge	AH	9.2	13.2	4.9	5.5	6.9
3-28	Formation discharge, 8A	AH	33.6	36.0	34.4	36.6	45.1
4-21	Cycle 2 discharge, 16A	AH	30.6	30.9	28.0	32.2	34.1
	Cycle 3 discharge, 2A	AH	27.9	31.3	31.3	33.0	45.9
4-30	Let down OCV	volts	.02	.18	.17	.16	.16
5--1	Heat sterilization		72 hours at 135°C sealed				
	Cycle 4 charge	AH	29.2	33.6	33.2	33.3	33.3
5-20	Cycle 4 discharge, 8A	AH	28.3	32.5	32.2	32.0	30.4
5-27	Cycle 5 discharge, 16A	AH	29.9	31.4	29.1	33.3	39.9
5-30	Cycle 6 discharge, 2A	AH	28.5	30.5	27.4	30.6	27.5
6-11	Cycle 7 discharge, 50A	AH	26.7	28.3	24.2	27.9	32.5
6-13	Cycle 8 discharge, 25A	AH	29.3	28.3	24.0	29.5	33.7
7- 3	Cycle 9 discharge, 8A	AH	24.0	24.0	20.1	26.1	27.7
8-25	(1st measuring cycle)						
	Test design output, 50% DOD	AH	11.2	10.1	10.4	11.9	12.8
	Number cycles completed	each	88	98	83	69	51
	Total discharge capacity on autocycles	AH	985	990	862	821	653
	Last 100% DOD cycle, 8A	AH	11.6	5	9.7	12.1	15.1
	Total discharge capacity (Auto & 100% DOD cycles)	AH	1244	1263	1113	1102	970

Notes: Cycles 1 through 9; 100% DOD; test rate to 1.25v/c at 70° ± 5°F.

TABLE V

SILVER PENETRATION OF 25 AH INTERMEDIATE CYCLE LIFE CELL SEPARATION

Cell S/N	Test Group	Design Group	Plate Wrap	Cycles to Failure (1)	Accum. Capacity AH	Failure Mode (2)	Type Separator, Layer, and Ag, mg/in^2										
								SWRI-GX Membrane									
							P	1	2	3	4	5	6	7	8	9	Total
	I	(No Pretest, No Platelock)															
3		1	+	168	1920	S	6.8	26.7	6.5	3.3	2.8	2.0	1.2	0.5	-	-	49.8
4		1	+	168	1920	NF	8.9	32.4	6.2	2.8	2.3	1.7	1.2	0.2	-	-	55.7
7		2	+	164	1690	NF	6.9	31.0	4.0	1.7	1.9	1.7	1.9	2.2	-	-	51.3
12		3	+	141	1480	C	-	25.5	13.3	8.1	1.4	1.2	1.3	1.6	0.7	0.2	53.3
14		4	-	127	1550	C	-	25.1	13.0	6.0	1.2	1.6	1.9	1.3	0.5	0.2	50.8
20		5	-	110	1440	C	-	23.0	14.1	7.1	1.3	1.3	1.2	1.3	1.3	1.1	51.7
	II	(Pretest, Double Bake-Out)															
2		1	+	88	1244	C	8.0	40.2	7.1	1.1	1.0	1.0	1.3	0.9	-	-	60.6
8		2	+	98	1263	S	10.8	44.9	4.0	0.9	0.9	0.8	1.1	2.4	-	-	65.9
11		3	+	83	1113	C	-	35.0	8.1	1.7	1.1	1.3	1.1	0.8	0.6	NT	49.8
15		4	-	69	1102	C	-	44.2	17.6	3.0	0.7	0.8	1.0	1.0	0.8	1.2	70.3
18		5	-	51	970	NF	-	49.3	13.7	2.9	0.5	0.5	0.6	0.7	0.7	1.0	69.9

(1) 10 hour charge/2 hour discharge C/3 rate on ESB cyclers (one-step) and/or DAS (2-step).
(2) Codes: NF = no failure; S = short; C = capacity below 50% rated.
(3) P = Pellon 2530 W absorber

TABLE VI

LIFE HISTORY OF 25 AH PLATE-LOCK CELL GROUP
(PRIOR TO ENVIRONMENTAL TESTS)

Test or Design Parameter	Unit	Observation by Cell S/N				
		21	22	23	24	25
1. Preformation Charge	AH	.67	.67	.67	.81	.81
2. Heat Sterilization 100 hours at 135°C		X	X	X	X	X
3. Formation Charge	AH	25.5	31.8	38.3	26.8	31.8
• Partial Discharge	AH	7.9	8.4	6.9	7.9	9.8
• Recharge	AH	12.6	14.1	10.4	14.5	15.4
• Net Input	AH	30.2	37.5	39.8	35.4	37.4
4. Formation Discharge 8A to 1.25V	AH	26.6	35.0	30.6	32.6	28.8
5. Cycle 2 Charge 1A to 2.03V	AH	23.6	28.3	23.6	26.6	28.3
6. Cycle 2 Discharge 16A to 1.25V	AH	22.0	30.1	28.8	24.0	27.5
Midvoltage	volts	1.44	1.44	1.43	1.47	1.44
7. Cycle 3 Charge 1A to 2.03V	AH	23.0	28.4	23.8	26.6	25.5
8. Cycle 3 Discharge 2A to 1.25V	AH	21.2	24.2	22.4	24.2	24.2
Midvoltage	volts	1.52	1.50	1.49	1.50	1.51
9. Cycle 4 Charge 1A to 2.03V	AH	25.9	26.7	26.7	23.1	26.3
10. Net Input, All Cycles	AH	32.9	31.6	32.1	30.9	37.6
11. Charged Stand at JPL	mos.	7.5	7.5	7.5	7.5	7.5
12. Cycle 4 Discharge	AH					
Step 1. 8A to 1.25V		19.3	23.3	20.9	20.5	22.1
Step 2. 2A to 1.25V		1.1	.9	.5	1.6	7.2
Total Output	AH	20.4	24.2	21.4	22.1	29.3

TABLE VI (Continued)

LIFE HISTORY OF 25 AH PLATE-LOCK CELL GROUP
(PRIOR TO ENVIRONMENTAL TESTS)

Test or Design Parameter	Unit	Observation by Cell S/N				
		21	22	23	24	25
13. Capacity Loss in 7.5 Months	AH	0.8	0	1.0	2.1	-5.1
% Loss vs Item 8	%	3.8	0	4.5	8.7	-
14. Capacity Loss in 9.0 Months	AH	7.3	11.7	9.7	12.1	6.7
% Loss vs Item 4	%	27.4	33.4	31.6	37.1	23.2
15. Cycle 5 Charge	AH	21.9	24.0	20.0	23.1	28.9
• Partial Discharge	AH	5.0	5.0	5.0	5.0	5.0
• Recharge Input	AH	11.7	11.4	8.7	7.6	8.8
• Net Input	AH	28.6	30.4	23.7	25.7	32.7
16. Cycle 5 Discharge						
Step 1. 8A to 1.25V	AH	26.0	27.2	23.2	24.9	25.7
Step 2. 2A to 1.25V	AH	.9	1.2	.8	1.9	2.6
Net Output, both steps	AH	26.9	28.4	24.0	26.8	28.3
17. Cycle 6 Charge	AH	27.8	28.0	18.8	26.8	27.2
• Partial Discharge	AH	5.0	5.0	3.0	5.0	5.0
• Recharge	AH	9.6	9.4	7.2	6.5	6.0
• Net Input	AH	32.4	32.4	22.9	28.3	28.2
18. Silver Active Weight Per Cell	g	88.7	80.9	82.2	94.5	103.7
19. Rated Capacity	AH	22	20	21	24	25
20. Separator System						
• Pellon 2530W		1L	1L	-	-	-
• SWRI-GX		7L	7L	9L	9L	9L
• Wrap		+	+	+	-	-
21. Negative Plate Density	g/in^3	49	42	42	42	49

FIGURE 1
AVERAGES BY THICKNESS LEVEL

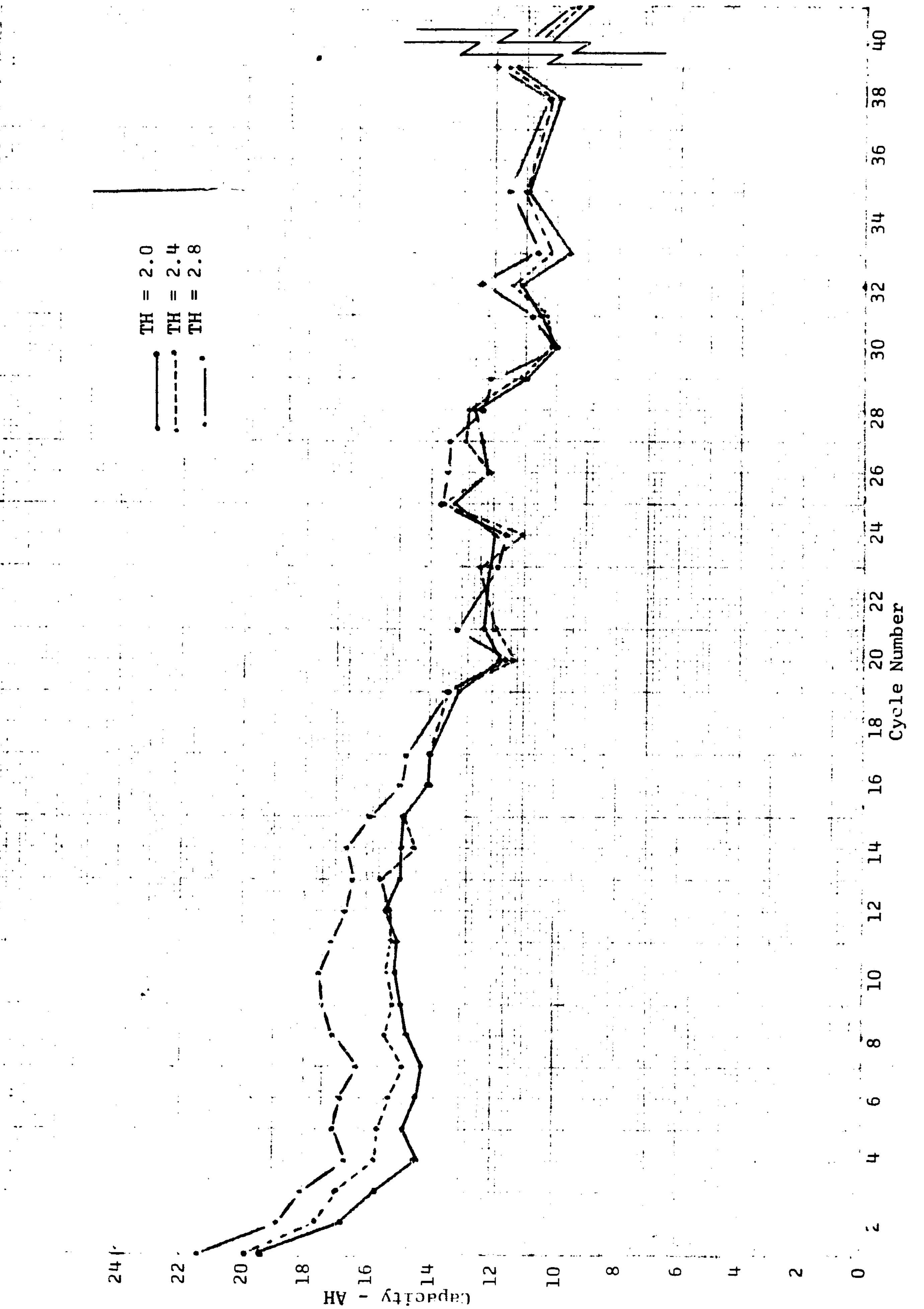


FIGURE 1
AVERAGES BY THICKNESS LEVEL

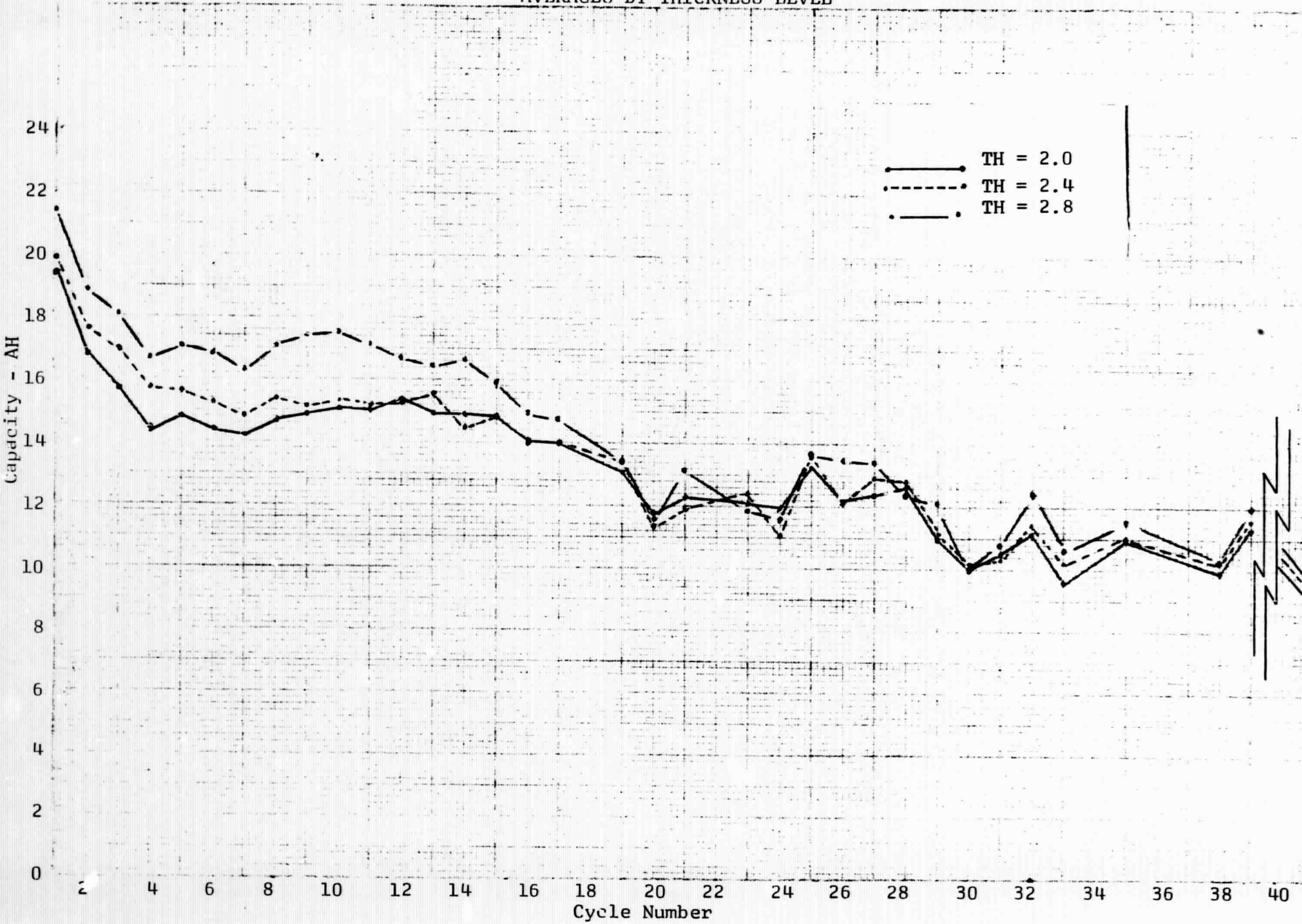


FIGURE 2
AVERAGES BY ZnO/Ag LEVELS

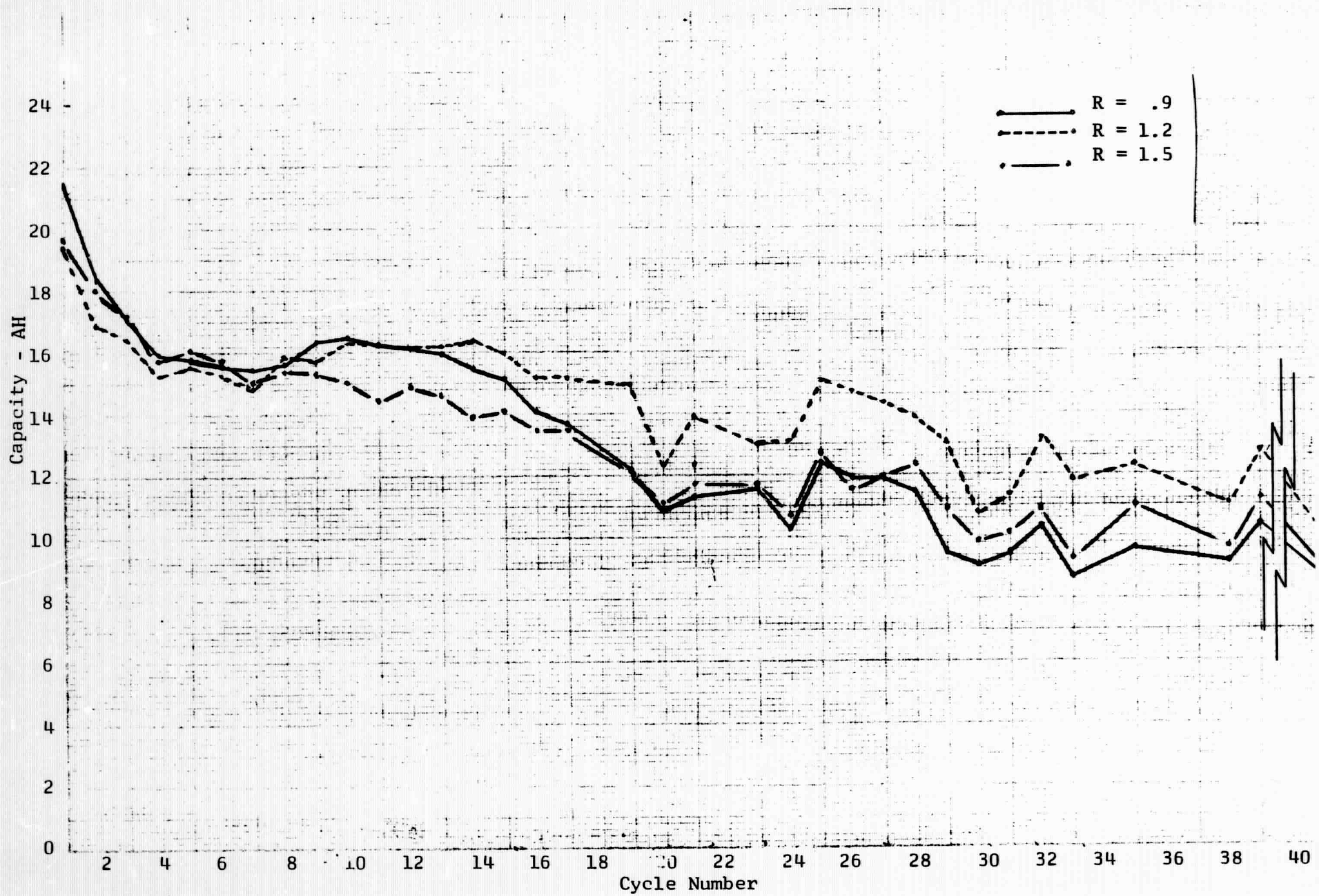


FIGURE 3
AVERAGES BY TEFLON LEVELS

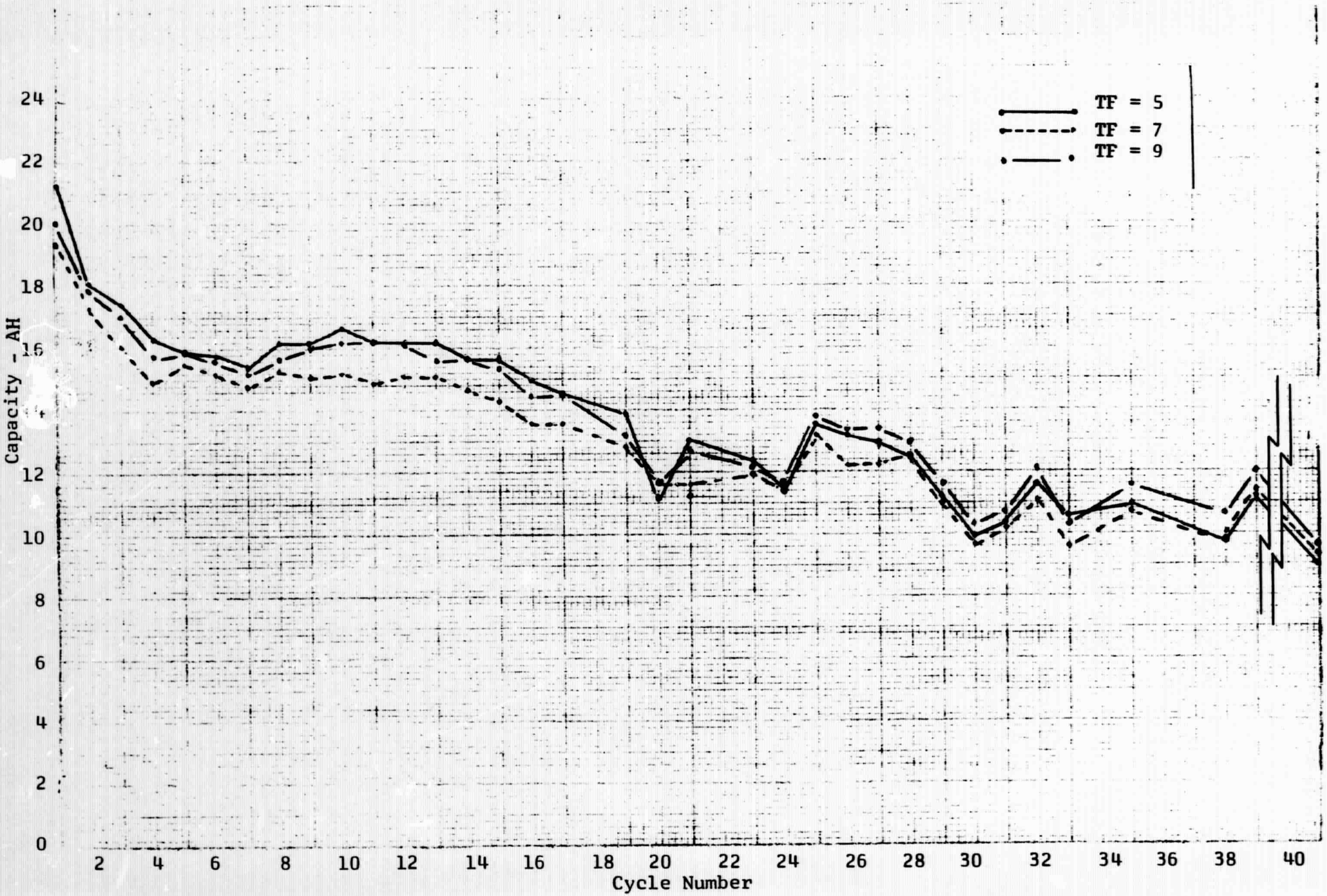


FIGURE 4
AVERAGES BY KOH LEVEL

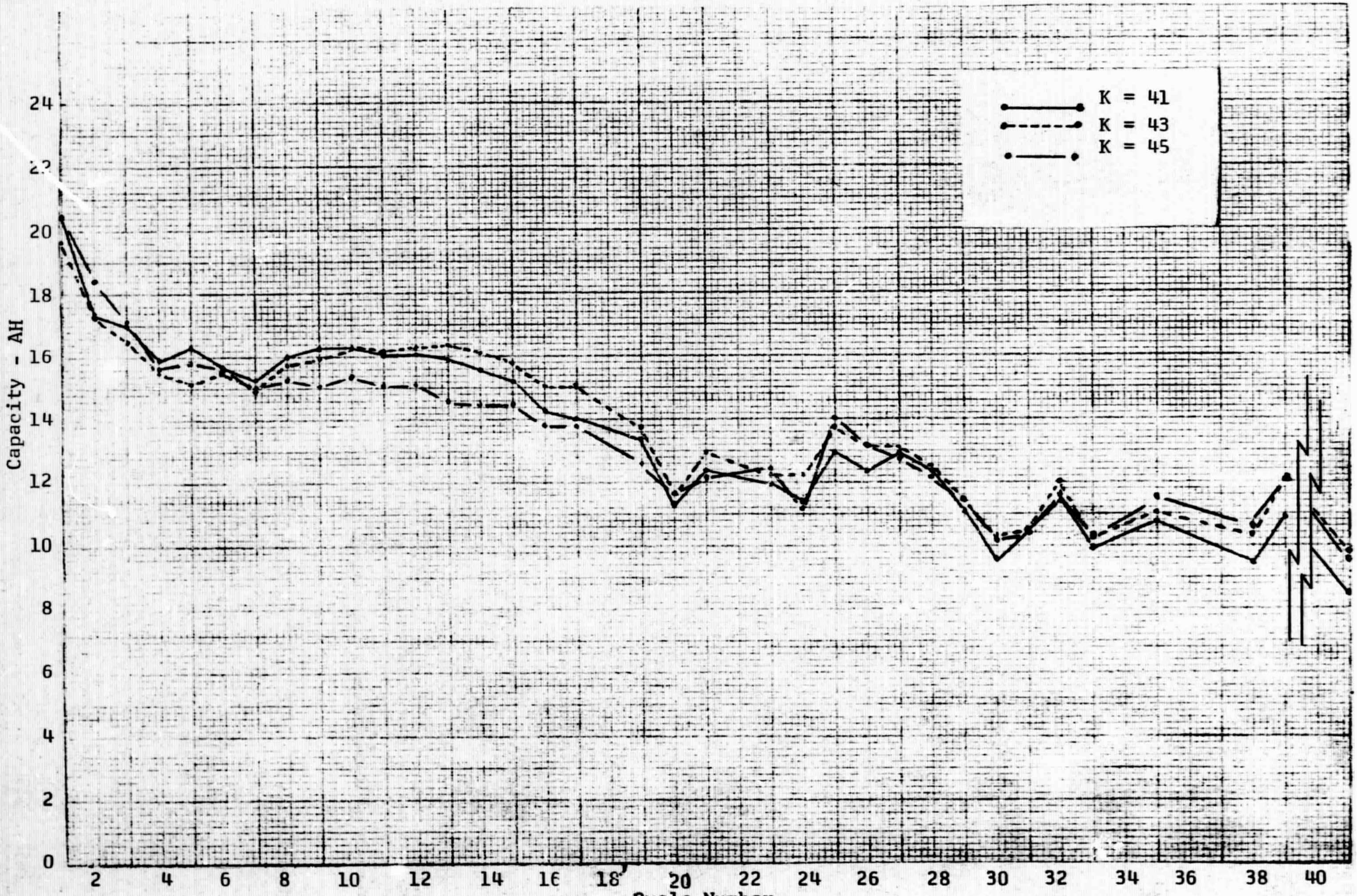
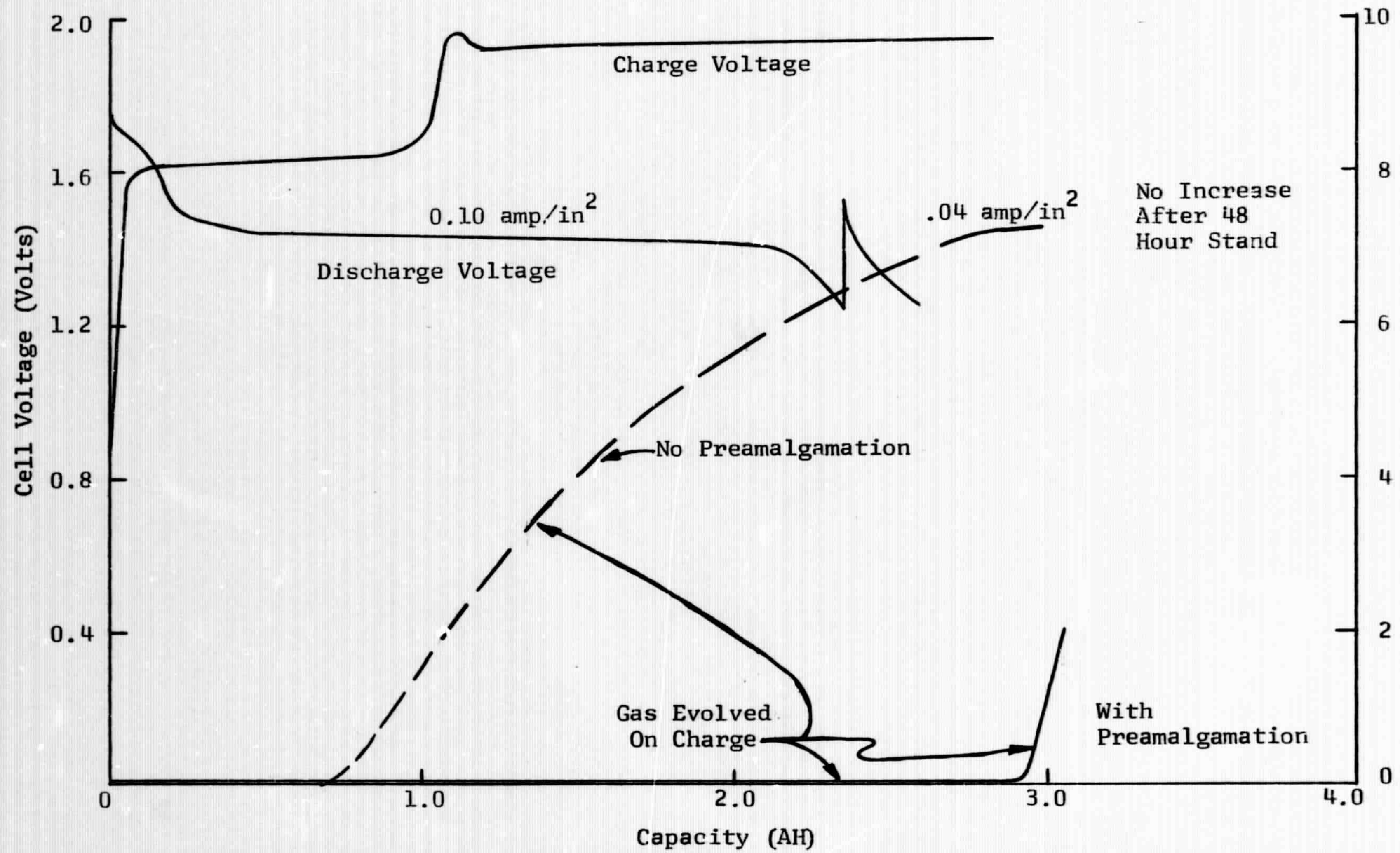


FIGURE 5

GASSING OF HIGH IMPACT NEGATIVE PLATES ON FORMATION CHARGE



References:

(1) Report for Second Quarter 1969, JPL Contract 951296, p. 37

(2) Report for Third Quarter 1969, JPL Contract 951296, p. 18

(3) Ibid, Table IV, p. 13.

A P P E N D I X

STATISTICAL ANALYSIS OF ESB CELL DEVELOPMENT EXPERIMENT

General

This report is based on data furnished by ESB to consulting statisticians R. J. Hader and A. H. E. Grandage of North Carolina State University. The data consist of discharge capacities through 53 charge - discharge cycles of 24 experimental cells. The experiment started with 27 cells representing a one-third replication of a 3^4 factorial experimental design. The four factors and their respective three levels were

Factor	Levels
Percent Teflon	5, 7, 9
Separator Thickness	2.0, 2.4, 2.8
ZnO/Ag Ratio	0.9, 1.2, 1.5
KOH Type	41, 43, 45

The statistical design used permits estimation of linear and quadratic effects (including interactions) of all four factors. Three cells were lost early in the experiment. Data from replacement cells is now available for the first 16 cycles, but this data was not used in the statistical analyses.

After 46 cycles the cells were modified by adding electrolyte to bring the electrolyte up to its original weight plus 5%.

The discharge capacities of each cell were plotted against cycle number. The results were quite variable but the general pattern was a sharp decrease for the first four or five cycles followed by a leveling off (or in some cells an actual increase) from cycles 5 through 15, then a gradual downward trend to cycle 46. After the addition of more electrolyte the capacities increased by percentages varying considerably from cell to cell. This aspect of the experiment was analyzed separately.

Superimposed on the general trends mentioned above were fluctuations which are highly correlated across all cells. These are apparently caused by some aspect of charging and discharging which affects all cells in a common way but varies from cycle to cycle.

Several cells had discharge capacities substantially lower than the majority. Some of these cases seem unrelated to the design variables in the sense that they do not appear to fall in any consistent pattern with respect to the design variables.

Analysis of Discharge Capacities at Particular Cycles

One set of statistical analyses consisted of an attempt to relate the capacity at a given cycle (or the average of three consecutive cycles) to the four design variables. Linear and quadratic regression models were fitted by least squares using the dependent variables C1, A5, ..., A45 listed in Table I and the independent variables shown in Table II. Through cycle 45 the only statistically significant effect detected in this group of analyses was the quadratic component of R (ZnO/Ag ratio) from the 15^{th} to the 45^{th} cycle. Cells at the middle level of R had significantly better performance than those at either the high or the low levels of R. This is shown graphically in the plot of discharge capacity averages against cycle number (Figure 1). The remaining plots of this type (Figures 2-4) show the lack of significant effects for the other three factors.

The quadratic effect of R was proven significant only after incorporation into the model of the covariate Δ = actual minus calculated electrolyte weight. This indicates that to some extent these small increments (which might be considered as measures of departure from intended design) do affect discharge capacities.

Analyses of Capacity Losses

In another set of analyses we attempted to relate differences (e.g. C1-A5, C1-A15, etc.) to the four design variables. Linear and quadratic regression models were fitted. Again the quadratic effect of R is evident and is significant either with or without the use of the covariate Δ. For differences C1-A15, C1-A20, etc. a significant interaction between TF and TH was also noted. From the two-way table of C1-A38 it appears that combinations of either low TH, high TF or high TH, low TF result in smaller capacity losses.

C1-A38 Averages

	TF = 5	TF = 7	TF = 9
TH = 2.0	12.4	8.6	6.5
TH = 2.4	10.1	6.4	9.5
TH = 2.8	8.9	10.5	10.2

However, in spite of its apparent statistical significance, we are inclined to distrust this conclusion. As each entry in the table is an average of at most 3 values, the results may be rather markedly influenced by one or two of the maverick cells. Further, a similar table of C1-A45 averages shows the effect much diminished and a formal analysis of (C1-A45)/C1 showed only R^2 significant.

Analysis of Changes After Adding Electrolyte

The third set of analyses concentrated on the effect of adding electrolyte after cycle 46. Discharge capacities increased for all but one cell. Several previously poorly performing cells at ZnO/Ag = 1.5 increased their discharge capacities to the point where the upper level of ZnO/Ag now has capacity values as high as (or slightly better) does the middle level of ZnO/Ag. In the regression analyses the significant quadratic effect of R is replaced by a significant linear effect of R. This would seem to indicate that insufficient electrolyte was a limiting factor for cells at ZnO/Ag = 1.5. At the lowest level of ZnO/Ag all but one cell showed capacity increases, however, the values remained generally below those for higher ZnO/Ag levels.

One further statistically significant effect appeared in this set of analyses. The difference A52-C48 was apparently influenced by TH. The following table shows how this arises

TH	A45	C48	A52	A52-C48
2.0	8.93	10.68	11.10	.42
2.4	9.38	11.85	11.25	-.60
2.8	9.53	12.06	11.27	-.79

It appears that, on the average, cells at TH = 2.4 and 2.8 had a somewhat larger gain in capacity on cycle 48 than did cells at TH=20. However, by cycle 52 the capacities were again approximately equal at all three TH levels.

Supporting Material and Graphical Presentation

Computer print-out for the regression analyses is submitted with this report. The print-out includes tables of averages for all independent variables classified by levels of each design factor and also according to each pair of design factors. The regression portion of the print-out includes "predicted" values for each cell for each model.

A series of three dimensional plots of selected dependent variables are appended to this report. On most of these the plot is against the three variables R, GX (i.e. TH) and KOH. The teflon levels may be superimposed on these plots by reference to the values in parenthesis on the plot showing cell numbers.

Conclusions.

(1) The only statistically significant effect of any design factor to cycle 45 before addition of electrolyte is the quadratic effect of the ZnO/Ag ratio. The middle level of ZnO/Ag has higher discharge capacities than the other two levels.

(2) After addition of 5% more electrolyte the capacities of cells at ZnO/Ag = 1.5 increase to the point where the linear effect of R becomes significant. The upper and middle levels are about equally good: however, the capacities are lower at ZnO/Ag = 0.9.

(3) Immediately after the addition of more electrolyte cells with TH = 2.4 and 2.8 had a greater increase in capacity than did those at TH = 2.0. However, at cycle 52 the capacities show no significant difference by levels of TH.

TABLE I

DEPENDENT VARIABLES ANALYZED

C1 =	discharge capacity for cycle 1					
A5 =	average	discharge	capacity	cycles	4, 5, 6
A15 =	"	"	"	"	14, 15, 16
A20 =	"	"	"	"	19, 20, 21
A27 =	"	"	"	"	26, 27, 28
A31 =	"	"	"	"	30, 31, 32
A38 =	"	"	"	"	35, 38, 39
A45	"	"	"	"	44, 45, 46
A49 =	"	"	"	"	48, 49, 50
A52 =	"	"	"	"	51, 52, 53

C1-A5	C1-A38	C48-A45
C1-A15	A5-A15	A49-A45
C1-A20	A5-A20	A52-A45
C1-A27	A5-A38	A52-C48
C1-A31	A15-A38	

Ratio 1 =	(C1-A45)/C1	Maintenance of Capacity
Ratio 2 =	(C48-A45)/A45	Electrolyte Effect
Ratio 3 =	(A52-A45)/A45	Retention of Capacity after 5% Electrolyte Addition

TABLE II
INDEPENDENT VARIABLES AND MODELS

$TF = (\text{Teflon} - 7)/2$

$TH = (\text{Thickness} - 2.4)/0.4$

$R = (ZnO/Ag - 1.2)/0.3$

$K = (KOH - 43)/2$

WTA = actual electrolyte weight

WTC = calculated electrolyte weight

Δ = DELWT = WTA-WTC

LINEAR MODELS

(1) Dependent Variable $= b_0 + b_1\,TF + b_2\,TH + b_3\,R + b_4\,K$

(2) Dependent Variable $= b_0 + b_1\,TF + b_2\,TH + b_3\,R + b_4\,K + b_5\,\Delta$

QUADRATIC MODELS

(1) Dependent Variable $= b_0 + b_1\,TF + b_2\,TH + b_3\,R + b_4\,K + b_5\,(TF)^2$

$+ b_6\,(TH)^2 + b_7\,R^2 + b_8\,K^2 + b_9\,(TF)(TH) + b_{10}\,(TF)(R)$

$+ b_{11}\,(TF)(K) + b_{12}\,(TH)(R) + b_{13}(TH)(K) + b_{14}(R)(K)$

(2) Dependent Variable $= b_0 + b_1\,TF + b_2\,TH + b_3\,R + b_4\,K + b_5\,(TF)^2$

$+ b_6(TH)^2 + b_7\,R^2 + b_8\,K^2 + b_9(TF)(TH) + b_{10}(TF)(R)$

$+ b_{11}(TF)(K) + b_{12}(TH)(R) + b_{13}(TH)(K) + b_{14}(R)(K)$

$+ b_{15}\,\Delta + b_{16}\Delta^2$

DEPENDENT VARIABLES ANALYZED

C1 =	discharge capacity for cycle 1							
A5 =	average	discharge	capacity	cycles	4,	5,	6
A15 =	"	"	"	"	14,	15,	16
A20 =	"	"	"	"	19,	20,	21
A27 =	"	"	"	"	26,	27,	28
A31 =	"	"	"	"	30,	31,	32
A38 =	"	"	"	"	35,	38,	39
A45 =	"	"	"	"	44,	45,	46
A49 =	"	"	"	"	48,	49,	50
A52 =	"	"	"	"	51,	52,	53

C1-A5	C1-A38	A5-A20
C1-A15	A5-A15	A49-A45
C1-A20	A5-A38	A52-A45
C1-A27	A15-A38	A52-C48
C1-A31	C48-A45	

Ratio 1 = (C1-A45)/C1

Ratio 2 = (C48-A45)/A45

Ratio 3 = (A52-A45)/A45

Figure 1
C1 = Discharge Capacity on First Cycle

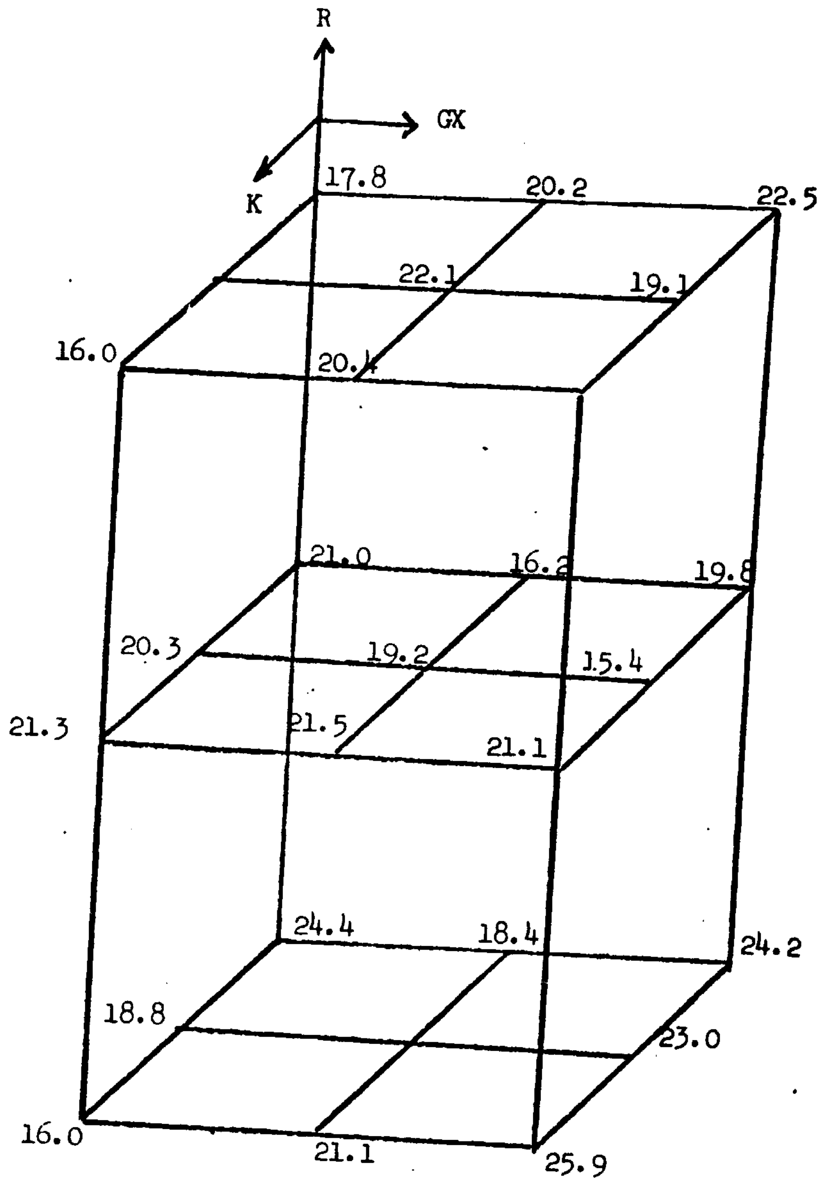


Figure 2
Percentage Capacity Loss Through Cycle 38

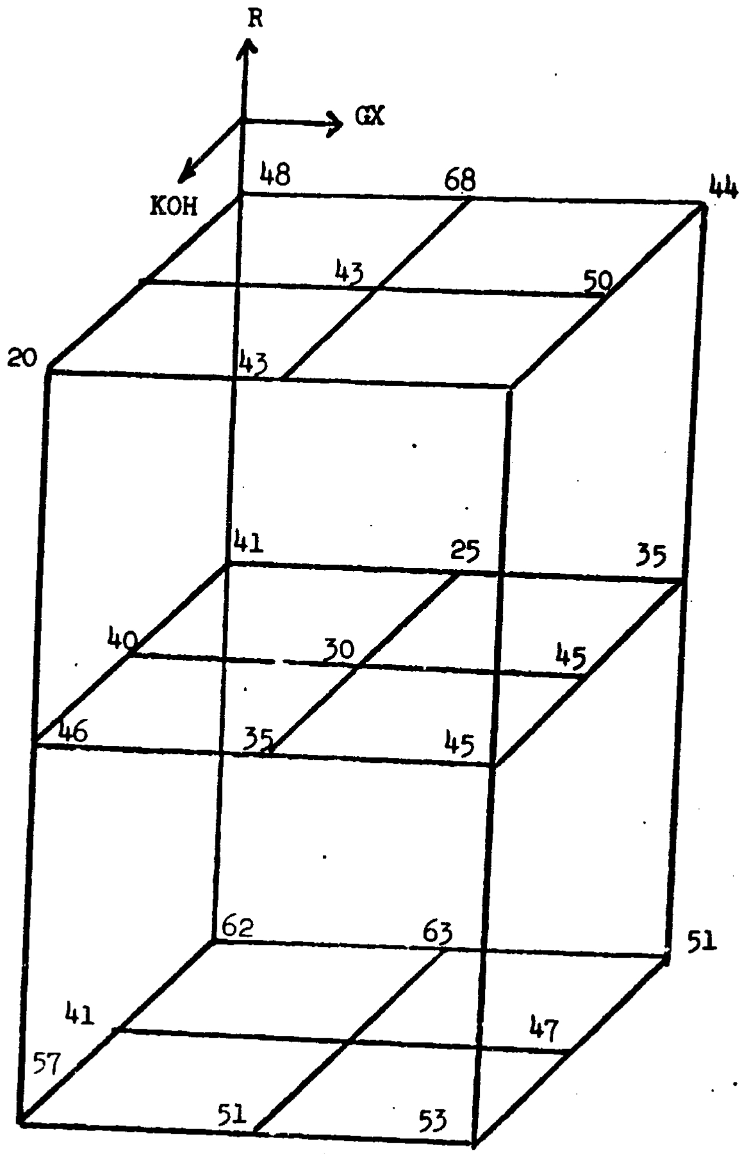


Figure 3
Percentage Capacity Loss Through Cycle 45

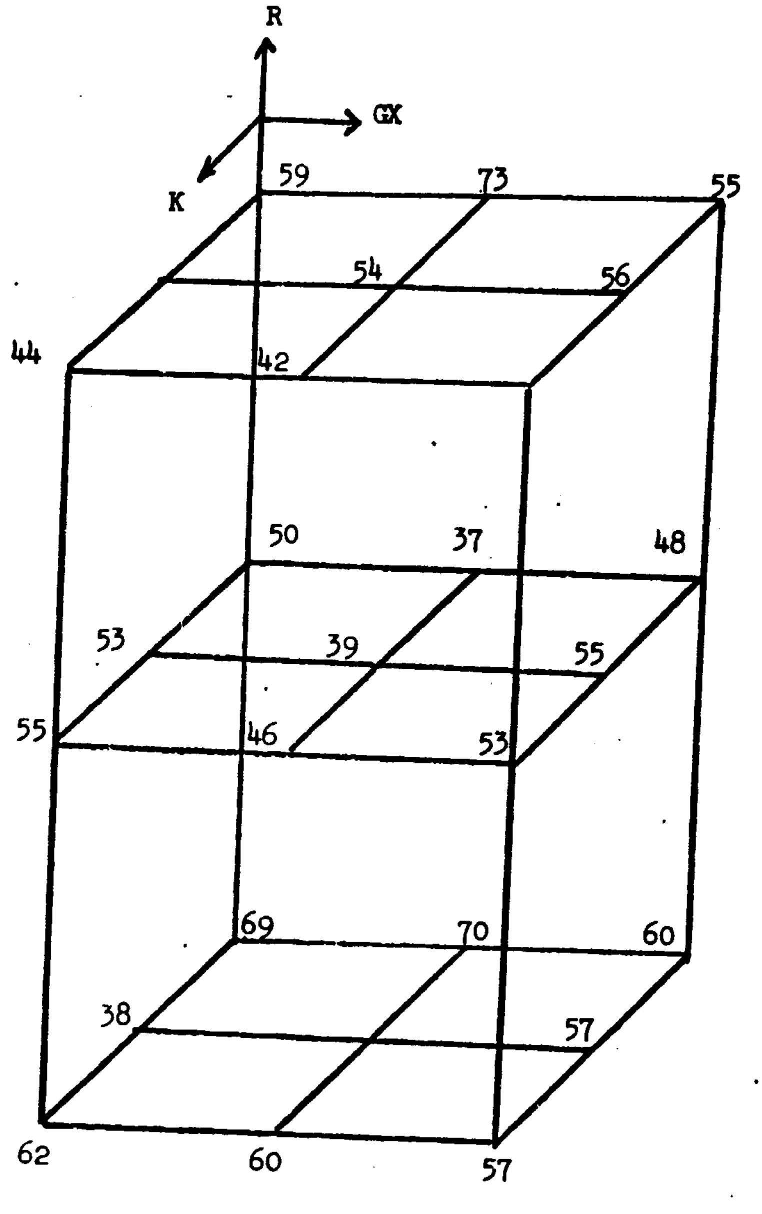


Figure 4
Percentage Capacity Increase Cycle 45 to Cycle 48

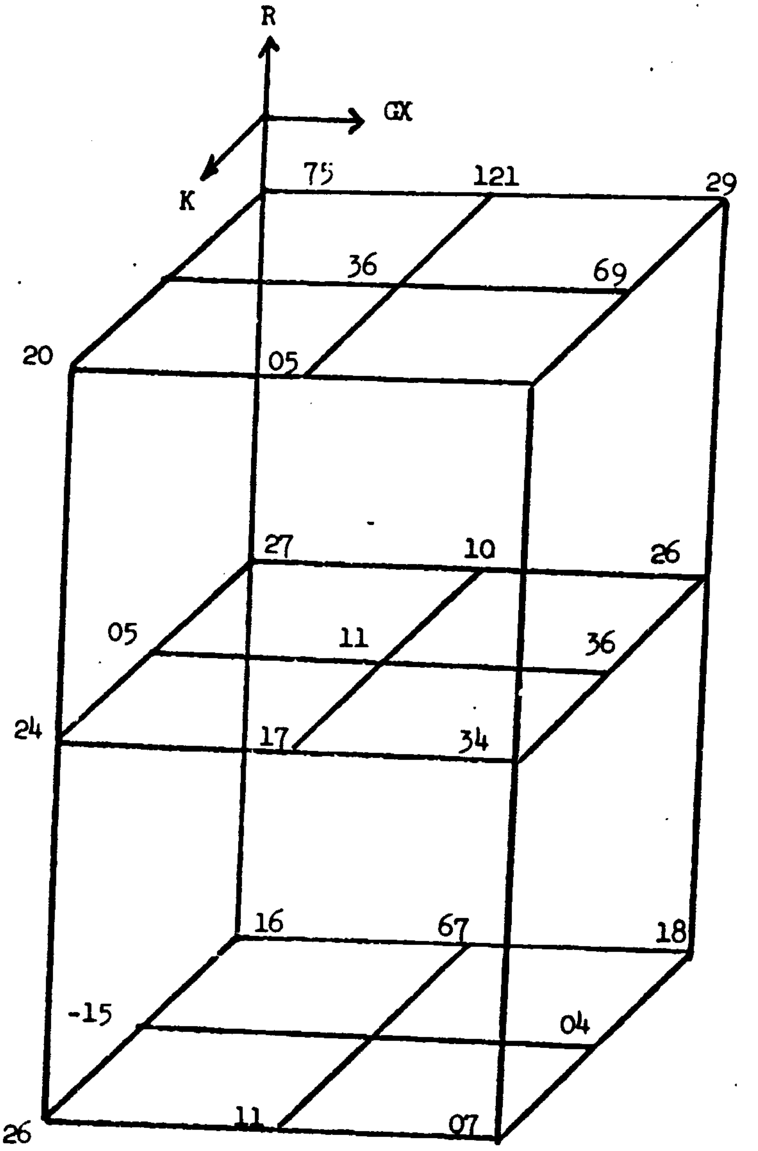


Figure 5
Percentage Capacity Increase Cycle 45 to Cycle 52